NOTES

ON

THERMODYNAMICS.

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PREFACE.

FOR the purpose of covering the theoretical side of thermodynamics more rapidly than could be done with the aid of existing text-books, the author prepared these notes four years ago for use in his classes.

The results were fairly satisfactory, and as the work is now used by other teachers, a revised edition has been prepared. In this, errors have been corrected, the text has been condensed, and additional problems have been added.

It is not intended as a reference-book, except for those who have worked it through and have solved the problems.

There is little that is new in it. All the later writers have been consulted in preparing the work, and whatever has seemed the most satisfactory method of arriving at a result has been made use of.

The work is not complete in itself, and a good table of the properties of vapors is required to work out many of the problems. The tables prepared by Professor Peabody are used in the text.

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NOTATION.

A = Heat equivalent of work = $\frac{1}{778}$.

c = Specific heat, the subscript indicating the law of the expansion, and is used whether units are foot-pounds or heat-units.

H = Heat required in heat-units or foot-pounds.

J = Mechanical equivalent of heat = 778.

K = Constant of equation $pv^n = K$.

λ = Total heat required to make 1 pound of vapor from liquid at 32 degrees F.

m = Weight.

M = Weight.

n = Exponent in equation $pv^n = K$.

p = Pressure in pounds per square foot, absolute.

q = Heat of liquid.

r = Total latent heat.

ρ = Inner latent heat.

R = Constant for any substance in equation $pv = RT$.

s = Volume of 1 pound of vapor.

σ = Volume of 1 pound of liquid.

t = Temperature Fahrenheit.

T = Temperature absolute.

u = Difference between the volume of 1 pound of vapor and 1 pound of liquid $= s - \sigma$.

v = Volume in cubic feet of 1 pound.

V = Any volume.

W = Work, foot-pounds or heat-units.

NOTES ON THERMODYNAMICS.

In Physics a distinction is made between perfect gases and vapors. In this work we will also deal with these two classes of substances, and, for engineering purposes, perfect gases are such as practically obey the laws of Boyle and Charles. Under the head of perfect gases would be classed air, hydrogen, oxygen, superheated steam, ammonia, carbonic acid, etc., all being sufficiently far from their condensing-point to obey the laws referred to above.

In the shape of a formula these laws can be best stated as

$$pv = RT. \qquad \qquad (1)$$

This equation is constantly being used in thermodynamics, and the exact meaning of the terms is important. In all this work English units, pounds, feet, and degrees Fahrenheit will be used. In these units the following definitions may be given to the terms of equation (1):

p is the absolute pressure in pounds per square foot.

v is the volume in cubic feet of 1 pound of the substance dealt with.

T is the absolute temperature, Fahrenheit degrees.

R is a constant whose value depends on the substance and the units taken.

To determine the value of R for any substance, we must have for one given condition of pressure and temperature the corresponding value of the volume of 1 pound. This we have for many substances. Thus, for air we have, for a pressure of 14.7 pounds per square inch, or $p = 14.7 \times 144$, and a temperature of 32 degrees Fahrenheit, or $T = 492.7$, the volume of 1 pound of air, or $v = 12.39$ cubic feet. These are quantities determined by experiment. Putting these values in equation (1), we have for air

$$R = \frac{pv}{T} = \frac{14.7 \times 144 \times 12.39}{492.7} = 53.37,$$

or, for air, with the units we have taken, we have

$$pv = 53.37T.$$

This equation is *always* true for air, and if, at any time or under any conditions, two of the variables in the equation are given, the third can be found.

Problem 1.—10 pounds of air at 200 degrees F. occupy 120 cubic feet; what must be the pressure?

$$\text{Here } T = 460.7 + 200 = 660.7\,; \quad v = \frac{120}{10} = 12\,;$$

$$p = \frac{53.37 \times 660.7}{12} = 2950 \text{ pounds per square foot.*}$$

Prob. 2.—How many pounds of air does it take to fill 5600 cubic feet at 15 pounds pressure per square inch and at 60 degrees F.?

* The slide-rule or three-place logarithms are used in the solution of all problems, and the result is probably correct within 2%.

Here $p = 15 \times 144$; $T = 460.7 + 60 = 520.7$;

$$v = \frac{520.7 \times 53.37}{15 \times 144} = 12.9,$$ and as this is the volume of 1 pound, 5600 cubic feet contain $\frac{5600}{12.9} = 434$ pounds of air.

Prob. 3.—At what temperature will 10 pounds of air at 15 pounds pressure per square inch fill 60 cubic feet?

Prob. 4.—What must be the pressure in a vessel of 4 cubic feet if it contains 30 pounds of air at 50 degrees F.?

Evidently, if, in equation (1), we are dealing with a substance twice as heavy as air, the value of v in the first member, or the volume of a pound, will be only half as great and, consequently, the value of R would be only half as great.

Substance.*	Relative Density.		*R* Value.
Air	14.4	53.37	53.4
O	16	$\frac{14.4}{16} \times 53.37$	48.1
H	1	14.4×53.37	770
N	14	$\frac{14.4}{14} \times 53.37$	54.9
CO_2	22	$\frac{14.4}{22} \times 53.37$	35.0
NH_3	8.5	$\frac{14.4}{8.5} \times 53.37$	90.6
CO	14	$\frac{14.4}{14} \times 53.37$	54.9
H_2O (steam)	9	$\frac{14.4}{9} \times 53.37$	85.6

* Some of these substances do not act as perfect gases at usual pressures and temperatures, so that care must be exercised in using these constants.

This enables us to apply the formula of equation (1) and its constant, as determined for air, to many other substances. From a table of relative densities one can readily determine the value of R for these substances, as in the table on page 3, and these values are practically correct for engineering calculations.

Prob. 5.—How many pounds of oxygen will a holder contain whose volume is 3 cubic feet, pressure 250 pounds per square inch, and temperature 75 degrees F.?

We have for oxygen

$$R = \frac{14.4 \times 53.37}{16}; \quad T = 460.7 + 75 = 535.7;$$

$$p = 250 \times 144 = 36000;$$

$$v = \frac{\dfrac{14.4 \times 53.37}{16} \times 535.7}{36000} \text{ and}$$

$$\text{wt.} = \frac{3 \times 36000 \times 16}{14.4 \times 53.37 \times 535.7} = 4.2 \text{ lbs.}$$

Prob. 6.—What weight of hydrogen will fill a holder of 3.5 cubic feet at 200 pounds pressure and $t = 80$ degrees F.?

Prob. 7.—What is the temperature at which a cubic foot of CO_2 will weigh .2 pound at 100 pounds pressure?

It is convenient to reduce the expression for the weight to a simple formula. If V is the total volume and v the volume per pound, then

$$\frac{V}{v} = \text{weight, or } M = \frac{pV}{RT},$$

from which of course, if $V = v$, the weight is 1 pound.

Prob. 8.—How many pounds of air will fill a vessel of 400 cubic feet at 15 pounds pressure if one-half the volume is at 80 degrees F. and the rest at 600 degrees F.?

The weight of the portion at 80 degrees is

$$M_1 = \frac{15 \times 144 \times 200}{53.37 \times 541} = 14.9,$$

and the weight of the remainder is

$$M_2 = \frac{15 \times 144 \times 200}{53.37 \times 1061} = 7.62.$$

The total weight is 22.65 pounds.

Prob. 9.—What must be the pressure at which 20 pounds of air will fill 270 cubic feet, 180 cubic feet being at 500 degrees and 90 cubic feet at 60 degrees F.?

In defining a perfect gas, there was one peculiarity which was not mentioned and which will now be of use. When a perfect gas is allowed to remain at the same temperature while its volume changes, the amount of heat that must be added to it to change its pressure and volume is that required to do the external work and no more. That is, if a perfect gas is allowed to expand and change its temperature, the quantity of heat which must be added to it is that required to change the temperature, added to that required to do external work.

As the equation $pv = RT$ contains three variables, it is not convenient to indicate all the variations of p, v, and T on the same diagram, and for convenience of representation, and because a diagram whose co-ordinates are pressure and volume is a diagram of work, the p, v co-ordinates will be understood unless different co-ordinates are marked on the figure.

Thus, in Fig. 1 if we call the two axes pressure and volume, and we have a pound of gas in the conditions represented by a, its volume is oy and its pressure is ay, the temperature being fixed from the equation $pv = RT$. If now the pressure of the gas is increased from ay to by, there being no change in volume, there will be no work done by the air. As its pressure is increased the temperature is increased in the same proportion, and we must have added enough heat to cause this change in temperature. If, however, instead of increasing the pressure, it had been maintained constant and the volume increased from oy to ox, we would have had not only to raise the temperature, but to have done work overcoming a pressure ay through a distance yx.

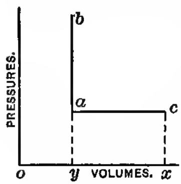

FIG. 1.

Again, if neither the pressure nor the volume remains constant, we have in Fig. 2 the condition a for the initial condition and d for the final condition, and the amount of heat which must have been added from a to d must have been enough to change the temperature from that at a to that at d, and also to do an amount of work equal to the area $ayxd$.

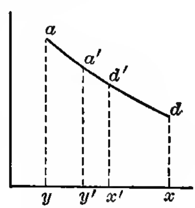

FIG. 2.

To express the relation between these quantities we must have units in which to measure them.

The unit in which the quantity of heat is measured is the amount of heat which must be added to 1

pound of water at 62 degrees F. to raise its temperature to 63 degrees, and is called the British Thermal Unit, or simply B.T.U.

The unit of work is the foot-pound, and, experimentally, it has been determined that one B.T.U. is equivalent to 778 foot-pounds.

The number of heat-units which must be added to 1 pound of any substance to raise it 1 degree in temperature is called the specific heat.

Referring now to Fig. 1, if c_v is the amount of heat which must be added per degree to raise the temperature from a to b, then c_v is the specific heat for constant volume, and the total heat required is $c_v(T_b - T_a)$ when T_b and T_a are the temperatures corresponding to the conditions b and a respectively. The value c_v for air is .169 heat-unit, or 132 foot-pounds.

Prob. 10.—If 5 cubic feet of air at 30 pounds pressure per square inch and 60 degrees F. has 20 heat-units added to it at constant volume, and if the heat required to raise the temperature of 1 pound 1 degree at constant volume is .169 heat-unit, what is the resulting temperature?

The weight of air is $\frac{5 \times 30 \times 144}{53.37 \times 521} = .774$ pound. The heat required to raise this 1 degree is $.774 \times .169 = .131$ heat-unit. The *rise* in temperature is therefore $\frac{20}{.131} = 153$ degrees.

Prob. 11.—If 15 cubic feet of air at 100 pounds pressure per square inch is raised from 60 degrees to 100 degrees F. at constant volume, how much heat is required?

Similarly, if c_p is the *total* amount of heat per degree which must be added to the pound of gas at a, Fig. 1, to cause the gas to expand from a to c, then c_p is the specific heat for constant pressure, and the total heat required is $c_p(T_c - T_a)$. In this case, however, the heat has been used partly in raising the temperature, the remainder being required to do external work. We can therefore write for the quantity required to change the temperature only, $c_v(T_c - T_a)$, and for the quantity required to do the work, $ay(ox - oy)$ or $p_a(v_c - v_a)$, and, as all the heat must be accounted for, we can write

$$c_p(T_c - T_a) = c_v(T_c - T_a) + p_a(v_c - v_a). \quad . \quad . \quad (2)$$

For air c_p is .238 heat-unit, or 185 foot-pounds.

Prob. 12.—If 1 pound of air is changed from 20 degrees to 30 degrees F. at a constant pressure of 100 pounds per square inch, how much heat must be added if to raise the temperature alone required that the equivalent of 132 foot-pounds of work be added for each degree?

The heat to change the temperature *only* is the equivalent of $(30 - 20) \times 132 = 1320$ foot-pounds. The amount of work to be done is to overcome the pressure of 100×144 pounds per square foot through the difference in volume. The initial volume is $\dfrac{53.37 \times 481}{100 \times 144} = 1.79$ and the final volume $= \dfrac{53.37 \times 491}{100 \times 144} = 1.83$. The work is then $100 \times 144(1.83 - 1.79) = 576.0$ foot-pounds. The total heat required is therefore the equivalent of $1320 + 576 = 1896$ foot-pounds.

Prob. 13.—If $c_v = 132$ foot-pounds, prove, by using equation (2), that $c_p = 185$ foot-pounds.

Taking now the third case, if we call c_n the total amount of heat per degree which must be supplied from a to d, Fig. 2, then c_n is the specific heat for the law represented in the figure. This is used up partly in changing the temperature, which will account for the amount $c_v(T_d - T_a)$, and the balance in doing the work represented by the area $ayxd$. We can therefore write

$$c_n(T_d - T_a) = c_v(T_d - T_a) + ayxd. \quad . \quad . \quad (3)$$

The two equations above can be written in the general form,

Total Heat =

Heat required to raise temperature + work done,

or, in the differential form,

$$dH = c_v dt + pdv, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

the latter term being the calculus method of indicating the elementary area $a'y'x'd'$.

This equation is the fundamental one of the thermodynamics of gases.

Equation (2) can be written as below from the fact that $p_c v_c = RT_c$, and $p_a v_a = RT_a$:

$$c_p(T_c - T_a) = c_v(T_c - T_a) + R(T_c - T_a),$$

or

$$c_p = c_v + R. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

This equation represents the relation between the quantities which it is important to remember.

Experimentally, it has been shown that, for perfect gases,

$$\frac{c_p}{c_v} = 1.41,$$

and we can write

$$c_p : c_v : R :: 1.41 : 1 : .41,$$

or

Heat added at constant pressure : Heat required to raise the temperature : the work done :: 1.41 : 1 : .41.

Prob. 14.—If 5 pounds of air at 170 degrees F. has 16 heat-units added to it at constant pressure, how much work is done? What is the final temperature?

To find the work done we have $5 \times c_p(t_2 - 170)$

$$= 16 \text{ h. u.}$$

$$\text{Work} = 5 \times R(t_2 - 170) = \frac{.41}{1.41} \times 16 \times 778 \text{ ft.-lbs.}$$

$$= 3620 \text{ ft.-lbs.}$$

$$\text{The rise in temperature} = \frac{\text{Work}}{5R} = \frac{3620}{5 \times 53.37} = 13^\circ.6.$$

The final temperature is $170 + 13.6 = 183.6$.

Prob. 15.—A given weight of air expanding at constant pressure does 1000 foot-pounds of work. What heat must have been added to the air? How much heat was used to raise the temperature?

Prob. 16.—15 cubic feet of air expands to 40 cubic feet under a constant pressure of 30 pounds per square inch. How much heat was required?

Now $pv = RT$, and if all are variables, we can write

$$pdv + vdp = Rdt,$$

and substituting this value of pdv in (4), we have

$$dH = c_v dt + Rdt - vdp,$$

or, from (5),

$$dH = c_p dt - vdp \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The two equations (4) and (6) are often spoken of as the two fundamental equations of the thermodynamics of perfect gases.

The quantity of heat required to cause 1 pound of air to expand doing work can then be written as follows:

$$H = c_v(T_2 - T_1) + \int_{v_1}^{v_2} pdv, \quad . \quad . \quad . \quad (7)$$

in which T_2 is the final temperature, v_2 the final volume, and T_1 and v_1 the corresponding initial conditions.

Prob. 17.—If the initial condition is such that 5 pounds of air occupy 50 cubic feet at 30 degrees F., and the final condition such that it occupies 120 cubic feet at 40 degrees F., and the expansion takes place along a straight line, how much work is done and how much heat added?

It is first necessary to find the pressure. From $pv = RT$ we have for the initial state, $p = \dfrac{53.37 \times 491}{\frac{50}{5}} = 2630$ pounds per square foot. For the final condition,

$p = \dfrac{53.37 \times 501}{\frac{120}{5}} = 1120$ pounds per square foot.

The work done is therefore, from a diagram,

$\dfrac{2630 + 1120}{2}(120 - 50) = 131000$ ft.-lbs. $= 168$ h. u.

The heat required to raise the temperature is

$$5 \times c_v(T_2 - T_1) = 5 \times \frac{53.37 \times 10}{.41 \times 778} = 8 \text{ h. u.},$$

and the total heat required is

$$168 + 8 = 176.$$

To determine the value of area *abcd* or the $\int_{v_1}^{v_2} pdv$,

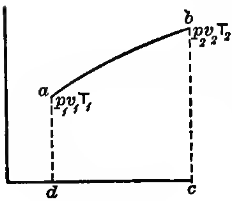

FIG. 3.

we must know the law connecting the pressure and the volume of the path *ab*. If we call this $pv^n = K$, we have, knowing p_1, v_1 and T_1, and p_2, v_2 and T_2,

$$p_1v_1^n = K, \quad p_2v_2^n = K,$$

$$\left(\frac{p_1}{p_2}\right) = \left(\frac{v_2}{v_1}\right)^n,$$

or
$$n = \frac{\log p_1 - \log p_2}{\log v_2 - \log v_1}. \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The value of K is obtained from either of the above equations.

Prob. 18.—What is the value of n that the expansion curve passing through the same initial and final points as in problem (17) should be $pv^n = K$?

$$\text{Area of } abcd = \int_{v_1}^{v_2} pdv = \int_{v_1}^{v_2} \frac{Kdv}{v^n} = \frac{K}{n-1}\left[-\frac{1}{v^{n-1}}\right]_{v_1}^{v_2}$$

$$= \frac{K}{n-1}\left[\frac{1}{v_1^{n-1}} - \frac{1}{v_2^{n-1}}\right].$$

Putting in the value of K for the equation above, we have the work

$$W = \frac{1}{n-1}(p_1v_1 - p_2v_2) = \frac{1}{n-1}(RT_1 - RT_2)$$

$$= \frac{R}{1-n}(T_2 - T_1). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Prob. 19.—Having given, in problem (17), that the law of the expansion is $pv^{.975} = K$, how much work is done if the final condition is $t = 40°$?

$$\text{Work} = 5 \times \frac{53.37}{1 - .975}(40 - 30) = 107000 \text{ ft.-lbs.}$$

The total quantity of heat required is therefore

$$H = c_v(T_2 - T_1) + \frac{R}{1-n}(T_2 - T_1). \quad . \quad . \quad . \quad (10)$$

$$= \frac{c_v - nc_v + R}{1-n}(T_2 - T_1) = \frac{c_p - nc_v}{1-n}(T_2 - T_1)$$

$$= c_n(T_2 - T_1),$$

when c_n is the specific heat according to the law $pv^n = K$.

Equation (10) is worth committing to memory as it is here given.

Prob. 20.—How much heat would be required in problem (19)? From problem (17) the heat required to change the temperature is 8 heat-units. From (19) the work done $= \frac{107000}{778} = 137$ heat-units. The total heat required is $137 + 8 = 145$ heat-units.

The special cases already treated of and some others may readily be derived from equations (9) and (10).

In $n = 0$, $pv^n = K$ becomes $p =$ constant, the work done, from (9), is, evidently, $R(T_2 - T_1)$, and the heat required, from (10), is $(c_v + R)(T_2 - T_1) = c_p(T_2 - T_1)$ as before.

If $\frac{1}{n} = 0$, we have $v =$ constant, and the work done, from (9), is evidently 0, as

$$\frac{\frac{R}{n}}{\frac{1}{n} - 1}(T_2 - T_1) = 0.$$

The heat required, from (10), is $c_v(T_2 - T_1)$.

If the heat is constant, we have $\frac{c_p - nc_v}{1 - n}(T_2 - T_1) = 0$, and one solution of this is $\frac{c_p}{c_v} = n$. This expansion, where no heat is added nor taken away but work is done, is called *adiabatic* expansion, and its equation is $pv^{\frac{c_p}{c_v}} = K$, or, as for air $\frac{c_p}{c_v} = 1.41$, we have

$$pv^{1.41} = K. \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

The work done is

$$\frac{R}{1 - n}(T_2 - T_1) = \frac{R}{.41}(T_1 - T_2).$$

Evidently, as $c_p = R + c_v$, and $c_p = 1.41c_v$, we have $R = .41c_v$, and the work done is, for adiabatic expansion, $c_v(T_2 - T_1)$, and the heat given up is $c_v(T_2 - T_1)$ to do this work.

If the temperature is kept constant we have $T_1 = T_2$, $pv = RT = K$, and $n = 1$. The amount of heat required is then, from equation (9),

$$\frac{c_p - c_v}{1 - 1}(T_2 - T_2) = \frac{0}{0},$$

which is indeterminate. We can, however, determine the quantity of work done and of heat added by going back to the original equation,

$$H = c_v(T_2 - T_1) + \int_{v_1}^{v_2} pdv.$$

Here $T_2 = T_1$ and $pv = K$. Consequently

$$H = \int_{v_1}^{v_2} pdv = \int_{v_1}^{v_2} \frac{Kdv}{v} = K \log_e \frac{v_2}{v_1} = p_1v_1 \log_e \frac{v_2}{v_1}. \quad (12)$$

Evidently, from the equation $pv = RT$, we can put RT_1 for either p_1v_1 or p_2v_2, and, from $pv = K$, we can put for $\frac{v_2}{v_1}$ the value $\frac{p_1}{p_2}$. In solving problems, that form of equation should be used which covers the greatest amount of given data.

Prob. 21.—If 1 pound of air has 40 heat-units added to it and 25 heat-units are the equivalent of the external work, what is the value of n in the equation $pv^n = K$?

As the external work $= 25$ h. u. $= \frac{R}{1-n}(T_2 - T_1)$, the remainder, 15 h. u., $= c_v(T_2 - T_1)$, or

$$\frac{15}{25} = \frac{c_v(1-n)}{R} = \frac{1-n}{.41}$$

$$n = .754.$$

Prob. 22.—If 10 heat-units are added to 1 pound of air at constant pressure, what work is done and what is the rise in temperature? We have

$c_p : c_v : R$ :: Heat added : Heat to raise temperature : work

$$:: 1.41 : 1 : .41 :: 10 : \frac{10}{1.41} : \frac{10 \times .41}{1.41}$$

$$\text{Work} = \frac{10 \times .41 \times 778}{1.41} = 2270 \text{ ft.-lbs.}$$

As we are dealing with 1 pound, the rise in temperature

$$= \frac{\text{Work}}{R} = 42.4 \text{ degrees.}$$

Prob. 23.—If 40 heat-units are added to 5 pounds of air having a pressure of 25 pounds per square inch and a volume of 30 cubic feet, what is: (1) final v, p, t; (2) the work done if (A) it is added at constant pressure, (B) at constant volume, (C) at constant temperature, (D) according to the law $pv^{\frac{1}{2}} = K$?

The value of n when no heat is added could have been determined directly from the fundamental equations as follows: When no heat is added we can write

$$dH = c_v dt + pdv = 0, \quad \text{or} \quad c_v dt = -pdv,$$

and

$$dH = c_p dt - vdp = 0, \quad \text{or} \quad c_p dt = vdp,$$

and dividing one by the other we have

$$\frac{c_v}{c_p} = -\frac{pdv}{vdp}, \quad \text{or} \quad \frac{c_v}{c_p} \cdot \frac{dp}{p} = -\frac{dv}{v},$$

or integrating between limits we have

$$\frac{c_v}{c_p} \log_e \left(\frac{p_1}{p_2}\right) = \log_e \left(\frac{v_2}{v_1}\right) = \log_e \left(\frac{p_1}{p_2}\right)^{\frac{c_v}{c_p}}$$

or, dropping the logarithms,

$$\frac{v_2}{v_1} = \left(\frac{p_1}{p_2}\right)^{\frac{c_v}{c_p}}, \quad \text{or} \quad p_1 v_1^{\frac{c_p}{c_v}} = p_2 v_2^{\frac{c_p}{c_v}}, \quad \text{or} \quad pv^{1.41} = K.$$

To determine whether the temperature will rise or fall during expansion, whether work must be done by the air or on the air, and whether heat must be added or taken away, Fig. 4 will be of service. Through

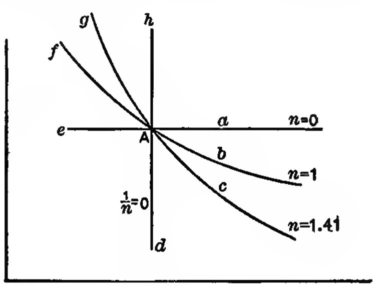

FIG. 4.

the initial point A, Fig. 4, we have drawn a series of curves for different values of n. $n = 0$ is at constant pressure, $\frac{1}{n} = 0$ is at constant volume, $n = 1$ is at constant temperature, and $n = 1.41$ is an adiabatic.

Evidently all expansion curves having n positive will

fall between a and d, all having n negative will fall between a and h. All compression curves having n positive will fall between e and h, and negative values will fall between d and e.

Starting at A, if the path of the air is to the right, work is done by the air, or is positive; if to the left, work is done on the air, or is negative. The following table should be mastered by the student. From A, then, calling rise in temperature, heat added, or work done by the air positive, we have, if curve falls between the limits,

	n.	Temp.	Heat.	Work.
a to b	$0 < n < 1$	+	+	+
b to c	$1 < n < 1.41$	−	+	+
c to d	$1.41 < n$	−	−	+
d to e	$n < 0$	−	−	−
e to f	$0 < n < 1$	−	−	−
f to g	$1 < n < 1.41$	+	−	−
g to h	$1.41 < n$	+	+	−
h to a	$n < 0$	+	+	+

We are now ready to take up the question of the amount of heat expended and the amount of work done when the gas under consideration goes through a series or cycle of changes, being at the end in the same condition as at the beginning. In Fig. 5, suppose we have a pound of the gas starting at the condition $p_1 v_1 T_1$ and expanding according to the law $pv^m = K$ until it reaches a point $p v_{2} T_2$. Suppose now it expands along the line

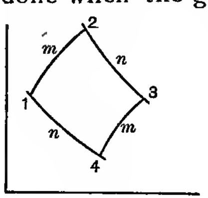

FIG. 5.

$pv^n = K_1$ to the condition $p_3v_3T_3$. It is then compressed along the line $pv^m = K_2$ to $p_4v_4T_4$, which is such a point that, if the compression is continued along the line $pv^n = K_3$, it will again reach its initial condition.

There are certain algebraic relations between the quantities in this diagram which should first be deduced. They are:

$$\frac{p_2}{p_1} = \frac{p_3}{p_4}; \quad \frac{v_2}{v_1} = \frac{v_3}{v_4}; \quad \frac{T_2}{T_1} = \frac{T_3}{T_4}.$$

From the given data we have

$$p_1v_1^m = p_2v_2^m; \; p_2v_2^n = p_3v_3^n; \; p_3v_3^m = p_4v_4^m; \; p_4v_4^n = p_1v_1^n,$$

and multiplying these equations together we have

$$v_1^m v_2^n v_3^m v_4^n = v_2^m v_3^n v_4^m v_1^n,$$

$$(v_1v_3)^{m-n} = (v_2v_4)^{m-n},$$

$$\frac{v}{v_1} = \frac{v_3}{v_4}. \quad \ldots \ldots \quad (13)$$

Again,

$$\frac{p_1}{p_2} = \left(\frac{v_2}{v_1}\right)^m; \quad \frac{p_3}{p_4} = \left(\frac{v_4}{v_3}\right)^m,$$

or

$$\frac{p_1p_3}{p_2p_4} = \left(\frac{v_2v_4}{v_1v_3}\right)^m = 1, \text{ from (13)};$$

$$\frac{p_2}{p_1} = \frac{p_3}{p_4}. \quad \ldots \ldots \quad (14)$$

Multiplying (13) by (14) we have

$$\frac{v_2p_2}{v_1p_1} = \frac{p_3v_3}{p_4v_4} = \frac{T_2}{T_1} = \frac{T_3}{T_4}. \quad \ldots \quad (15)$$

These relations should be kept in mind, as they often lead to an easy solution of problems. Equations

(13) and (14) are true if the figure is bounded by any two similar (algebraic) sets of curves, and equation (15) is only true for substances having $pv = RT$ for their equations.

The work done in a cycle similar to that in the figure is evidently the area of the diagram, or it is the heat added from 4 to 2, less that taken away from 2 to 4.

From 4 to 1,

$$\text{Heat} = \left(c_v + \frac{R}{1-n}\right)(T_1 - T_4); \qquad \text{Work} = \frac{R}{1-n}(T_1 - T_4).$$

From 1 to 2,

$$\text{Heat} = \left(c_v + \frac{R}{1-m}\right)(T_2 - T_1); \qquad \text{Work} = \frac{R}{1-m}(T_2 - T_1).$$

From 2 to 3,

$$\text{Heat} = \left(c_v + \frac{R}{1-n}\right)(T_3 - T_2); \qquad \text{Work} = \frac{R}{1-n}(T_3 - T_2).$$

From 3 to 4,

$$\text{Heat} = \left(c_v + \frac{R}{1-m}\right)(T_4 - T_3); \qquad \text{Work} = \frac{R}{1-m}(T_4 - T_3).$$

The net work done is therefore the area of the diagram, or

$$\frac{R}{1-n}(T_1 + T_3 - T_2 - T_4) + \frac{R}{1-m}(-T_1 - T_3 + T_2 + T_4)$$

$$= R\left(\frac{1}{1-n} - \frac{1}{1-m}\right)(T_1 + T_3 - T_2 - T_4).$$

The total quantity of heat which must be added is

that required to raise the body from T_4 to T_2 through T_1, or

$$\left(c_v + \frac{R}{1-n}\right)(T_1 - T_4) + \left(c_v + \frac{R}{1-m}\right)(T_2 - T_1)$$

= total heat added; or, calling c_m and c_n the specific heats according to the laws 1, 2 and 4, 1, we have

$$\text{Total heat} = c_n(T_1 - T_4) + c_m(T_2 - T_1).$$

The efficiency, which is the ratio of the work done to the heat expended, is then

$$\frac{R(-T_2 - T_4 + T_1 + T_3)\left(\frac{1}{1-n} - \frac{1}{1-m}\right)}{c_n(T_1 - T_4) + c_m(T_2 - T_1)}.$$

If either set of curves is adiabatic we have, say for $n = 1.41$, for the efficiency

$$\frac{R\left(-\frac{1}{1-m} - \frac{1}{.41}\right)(T_1 + T_3 - T_2 - T_4)}{c_m(T_2 - T_1)}.$$

As $R = .41c_v$, we have

$$-\frac{-T_2 - T_4 + T_1 + T_3}{T_2 - T_1},$$

$$1 - \frac{T_3 - T_4}{T_2 - T_1}.$$

Putting $T_3 = \frac{T_2 T_4}{T_1}$, we have for the efficiency

$$\frac{T_1 - T_4}{T_1} = \frac{T_2 - T_3}{T_2}. \quad . \quad . \quad . \quad . \quad (16)$$

That is, in any such cycle, the efficiency is the drop in temperature along either adiabatic divided by the highest temperature on that adiabatic. The amount of work done in such a cycle can be determined by multiplying the heat added by this efficiency.

Prob. 24.—A cycle is made up of two adiabatics and two curves $pv^{.5} = K$. If 10 heat-units are added to 1 pound of air, $p_1 = 3000$ pounds per square foot, $v_1 = 10$ cubic feet, how much work will be done, the lowest temperature in the cycle being 0 degrees F., and what is the highest temperature in the cycle?

In Fig. 6 we have the data given as shown. To determine T_1, we have $T_1 = \dfrac{3000 \times 10}{53.37} = 561$. The work done is

$$10 \times \frac{561 - 461}{561} \times 778 = 1390 \text{ ft.-lbs.}$$

To determine T_2, we know that 10 heat-units are added from T_1 to T_2 according to the law $pv^{.5} = K$, or

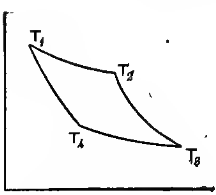

FIG. 6.

$$10 = \left(c_v + \frac{R}{1 - .5}\right)(T_2 - T_1)$$

$$= \frac{53.37}{778}\left(\frac{1}{.41} + \frac{1}{.5}\right)(T_2 - T_1).$$

$$T_2 - T_1 = 32.8, \quad T_2 = 593.8.$$

Prob. 25.—A cycle is made up of two isothermals and two constant-volume lines. The extreme volumes are 40 and 10 cubic feet, and the extreme pressures are 15 and 100 pounds per square inch. How much work is done and how much heat is required?

Prob. 26.—A cycle is made up of two constant-pressure and two isothermal lines. The extreme pressures are

15 and 10 pounds per square inch, and the extreme volumes are 10 and 70 cubic feet. How much work is done and how much heat is required?

Prob. 27.—Having given 2 pounds of air at $p_1 = 3000$ pounds, $v_1 = 15$ cubic feet, $T_2 = 460$, $T_3 = 420$, and $pv^{.7} = K$, how much work is done, the other curves being adiabatics?

In a cycle such as we have just been considering it can be shown that the work done may be expressed in a number of ways. In Fig. 7 the heat added from T_1 to $T_2 = c_n(T_2 - T_1) = Q_1$. The heat taken away from T_3 to T_4 $= c_n(T_3 - T_4) = Q_2$. The first of these divided by T_1 is equal to the second divided by T_4. For we have the relation

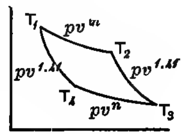

FIG. 7.

$$\frac{T_2}{T_1} = \frac{T_3}{T_4},$$

and, therefore,

$$\frac{T_2 - T_1}{T_1} = \frac{T_3 - T_4}{T_4},$$

$$\frac{c_n(T_2 - T_1)}{T_1} = \frac{c_n(T_3 - T_4)}{T_4}.$$

In the same way the heat along the top line divided by T_2 is equal to the heat along the bottom line divided by T_3. The work in such a cycle can therefore be stated as the heat added along either line divided by the temperature at either end of the line taken and multiplied by the range of tempera-

ture along the adiabatic passing through the point at which the temperature was taken, or the work is

$$\frac{Q_1}{T_1}(T_1 - T_4) = \frac{Q_1}{T_2}(T_2 - T_3) = \frac{Q_2}{T_4}(T_1 - T_4)$$

$$= \frac{Q_2}{T_3}(T_2 - T_3). \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

This relationship should be entirely understood.

Having shown that the work done in any cycle having adiabatic curves for two of the bounding curves is equal to the heat added times the range in temperature along one adiabatic divided by the maximum temperature along that adiabatic, it can be shown that, if the heat is added at constant temperature, the maximum range in the cycle being the same, the amount of work done or the efficiency will be the greatest. In Fig. 8 let 1, 2 and 3, 4 be isothermals, and 2, 3 and 1, 4 be adiabatics. Then 1 and 2 will be at the highest temperature, and 3 and 4 at the lowest. The efficiency is then $\frac{T_1 - T_4}{T_1}$. Now, suppose the heat, instead of being added along an isothermal, is added according to any law as 1, 5. The temperature of 5 is evidently below 1 or 2, as we have assumed that T_1 is the highest obtainable temperature. As T_3 is the lowest temperature, it is evident that a curve similar to 1, 5 passing through 3 will cut 1, 4 at a higher temperature than T_4. The efficiency is then

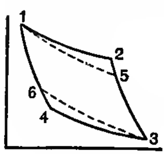

FIG. 8.

$\dfrac{T_1 - T_6}{T_1}$, which is evidently less than $\dfrac{T_1 - T_4}{T_1}$, as T_6 is greater than T_4. As the efficiency is less, the work done by the same quantity of heat is less. Therefore the greatest efficiency is obtained when heat is added at constant temperature, which also implies that heat must be taken away at constant temperature.

The diagrams we have drawn heretofore have shown the amount of work done, but have given us no graphical idea of the quantity of heat which enters the cycle. This quantity of heat, as well as the quantity of work, can be shown by a definite area on this diagram. By a definite area is meant one that can be measured by a planimeter.

Suppose 1, 2, Fig. 9, to be the path representing the changes in pressure and volume. We have the

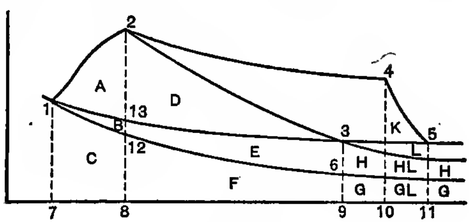

FIG. 9.

work done $A + B + C$, the letters referring to the spaces in which they occur.

At 1 the total energy in the gas can be represented by drawing the adiabatic 1, 12, 6 and continuing it indefinitely to the right. The area under this curve, or $C + F + G$, is the equivalent of the energy in the substance at 1, because it is the amount of work

which would be done if it was allowed to expand at the expense of its own heat until it reached the absolute zero. At 2 the energy remaining in the gas can be represented by the total area under the adiabatic 2, 3 drawn through 2. This is equal to $D+E+F+H+G$. We have then that the amount of heat added is equal to the energy remaining at 2 plus the work done from 1 to 2 and minus the energy at 1, or

Heat added

$$\begin{aligned}&=(D+E+F+H+G)+(A+B+C)-(C+F+G)\\&=A+B+D+E+H,\end{aligned}$$

or *the area between the path* 1, 2 *and two adiabatics drawn through the extremities of the path and indefinitely extended.*

We have already seen that the work done by a pound of air expanding adiabatically can be represented by

$$\frac{R}{1-1.41}(T_2-T_1),$$

where T_2 is the final and T_1 is the initial temperature. The energy in a pound of gas at 1 can be determined by making T_2 in the above equation 0, and $\frac{RT_1}{.41}$ or $\frac{p_1v_1}{.41}$ is the energy. Similarly at 2 the energy in a pound of the gas is $\frac{p_2v_2}{.41}$. If 2, 4 is an isothermal through 2, the energy in the gas at 2 is the same as at 4, or

$\frac{RT_2}{.41}$, and if 1, 3, 5 is an isothermal through 1, the energy in the gas at 1, 3, or 5 is

$$\frac{p_1 v_1}{.41} = \frac{RT_1}{.41}.$$

Evidently, if, after expansion takes place from 1 to 2, we allow it to continue adiabatically to 3, the air has as much energy at 3 as it had at 1, and whatever heat we have added has all gone to do work. The total work done is $(A + B + C + D + E + F)$, and this is equal to the heat added from 1 to 2.

The area $D + E + F$ is equal to the area $K + L$, for at 2 the energy in the gas is $\frac{RT_2}{.41}$, and at 4 it is the same. At 3 the energy is $\frac{RT_1}{.41}$, and at 5 it is the same. Passing from 2 to 3 the energy converted into work is $\frac{R}{.41}(T_2 - T_1)$, and from 4 to 5 it is the same. But the work done is in one case $D + E + F$, and in the other $K + L$; and as they are the equivalent of the same amount of energy, they are equal to each other.

Prob. 28.—How much energy is there in 1 pound of air after it has expanded adiabatically to 20 cubic feet, if its initial conditions were $p = 2000$ pounds, $v = 16$ cubic feet?

Prob. 29.—What is the energy in 10 cubic feet of oxygen at 100 pounds pressure per square inch and 100 degrees F.?

There is another method of illustrating graphically the heat added under any conditions. If we attempt to draw a diagram having absolute temperature T for ordinates and Q, the heat, for the area under any curve to the other axis of co-ordinates, the abscissa is $\int \frac{dQ}{T}$, because $Q = \int Td\left(\int \frac{dQ}{T}\right)$. The quantity $\int \frac{dQ}{T}$ is called entropy.

Evidently on such a diagram an adiabatic is represented by a line parallel to the T axis, because no heat is added along an adiabatic. The diagrams shown in Figs. 10 and 11 represent a p, v diagram and a T, $\int \frac{dQ}{T}$ diagram.

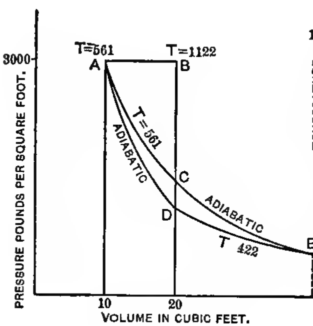

FIG. 10.

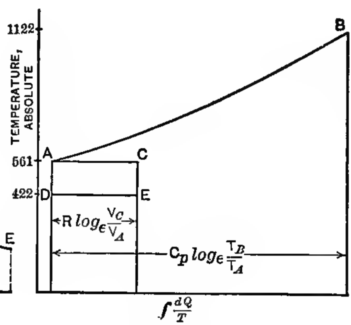

FIG. 11.

The data assumed in drawing these diagrams are $p_A = 3000$, $T_A = 561$, $v_A = 10$, $v_B = 20$; for AB, $n = 0$; AC, $n = 1$; AD, $n = 1.41$; CE, $n = 1.41$; and for DE, $n = 1$.

In locating points in Fig. 11, the point A is taken at any point on the $T = 561°$ line. To determine the distance to C, we have, as this is a constant-temperature line, $dQ = pdv$, and

$$\int \frac{dQ}{T} = \int \frac{pdv}{T} = R\int \frac{dv}{v} = R \log_e \frac{v_C}{v_A} = 37.1.$$

To locate the point B, we have $dQ = c_p dt$ and

$$\int \frac{dQ}{T} = \int \frac{c_p dt}{T} = c_p \log_e \frac{T_B}{T_A} = 128.$$

These diagrams are drawn to such a scale that the area represents foot-pounds in either diagram. In the first diagram, Fig. 10, the area under AB is the work done at constant pressure, and in the second diagram, Fig. 11, it is the heat added and is $\frac{1.41}{.41}$ as great. In the first the area under AC is the work done at constant temperature, and in the second it is the heat added and is exactly equal to it. In the first the area under AD is the work done adiabatically, and in the second it is zero, as it should be.

If we draw through D an isothermal as shown by the line DE, the point E completes a cycle, and for the second figure evidently $\frac{Q_{AC}}{T_{AC}} = \frac{Q_{DE}}{T_{DE}}$, as proved above, and the areas $ACED$ in the two figures are equal.

Prob. 30.—Draw diagrams, similar to Figs. 10 and 11, to scale representing the expansion of 1 pound of air

at 60 pounds pressure and 100 degrees F. (A) adiabatically, (B) along the isothermal, (C) at constant pressure, until the volume is doubled, and in each case, if possible, represent by a *definite* area the amount of work done and energy expended.

GENERAL EQUATIONS.

In taking up the portions of thermodynamics treating of substances generally, certain matters which we have already deduced apply, while certain others do not. Thus, Fig. 12, if AB is the path of the substance

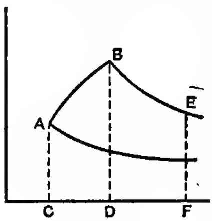

FIG. 12.

under discussion (any substance), the external work done is here, as before, the area $ABDC$. The total amount of head added to cause the substance to pass from A to B is again represented by the area between AB and two adiabatics at the extremities A and B indefinitely extended to the right. Here, however, the adiabatics are not necessarily curves whose equation is $pv^{1.41} = K$, as this relation only applies to perfect gases. They are curves, however, so drawn that from B to E, for instance, the area $BEFD$, which is the external work done, is the exact equivalent of the heat-energy which has disappeared as such between B and E.

We have called certain lines isothermals, and made certain statements about these lines. That is, in Fig. 13, if AB is an isothermal for a perfect gas, it is a rectangular hyperbola, the heat added from A to B is the area $L'BAL$ and is exactly equal to the area

ABCD representing the external work. Hereafter *AB*, if it is an isothermal, is *only* a line of constant temperature; it need not be and often *is not* a rectangular hyperbola. The heat added is equal to *L'BAL* but is *not* necessarily equal to *ABCD*.

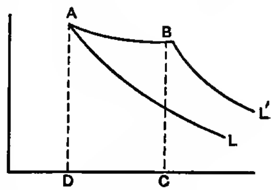

FIG. 13.

The work done *is* equal to *ABCD* and may or may not be equal to *L'BAL*.

The attempt will be made hereafter to use the terms *adiabatic* and *isothermal* in the general sense spoken of above.

Fig. 14 shows the work done, and Fig. 15 the heat added isothermally to any substance. In Fig. 14 the

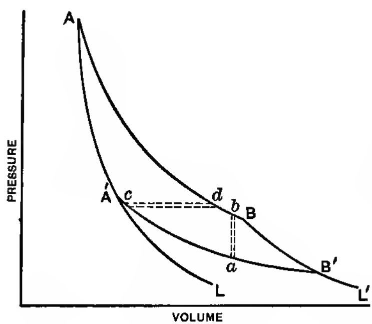

FIG. 14.

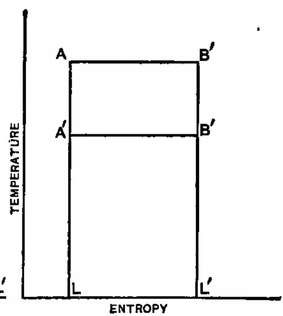

FIG. 15.

isothermal may be a rectangular hyperbola if we are dealing with air, a constant-pressure line if we are dealing with a mixture of liquid and vapor, or it is the line which represents the relation between p and v at con-

stant temperature. In Fig. 15 it must be a line perpendicular to the T axis. AL and B' are adiabatics; in Fig. 14 they are curves, and in Fig. 15 they must be straight lines parallel to the T axis. The heat H added from A to B in both diagrams is the area $ABL'L$. Draw any other isothermal $A'B'$ in both diagrams so that its temperature is dt degrees below AB. Evidently, from Fig. 15, the area $ABB'A'$ is equal to $\frac{H}{T}dt$. From Fig. 14, the equal area $ABB'A'$ is $\int dp\,dv$, and these two quantities are equal to each other, or

$$\frac{H}{T}dt = \int dp\,dv, \quad . \quad . \quad . \quad . \qquad (18)$$

where dp is the vertical distance between AB and $A'B'$, or dv is the horizontal distance between these lines, but not both at the same time. We can write the equation in either of the following forms:

$$\frac{H}{T}dt = \int_{v_A}^{v_B}(dp)\,dv = \int_{p_A}^{p_B}(dv)dp,$$

the quantity in the parenthesis meaning that the value of (dp) is fixed by the isothermals and that dv is the other independent variable, or in the last member the reverse is the case.

As it is the quantity ab in Fig. 14 that we must

insert in the equation for (dp), we can determine its value from the equation of the substance by determining $\left(\frac{\Delta p}{\Delta t}\right)_v$,* which gives us the rate of charge of p with T, and multiplying this by dt, or $ab = \left(\frac{\Delta p}{\Delta t}\right)_v dt$. Similarly $(dv) = cd = \left(\frac{\Delta v}{\Delta t}\right)_p dt$, or writing these values in the original equations, we have

$$\frac{H}{T}\,dt = \int_{v_A}^{v_B}\left(\frac{\Delta p}{\Delta t}\right)_v dt\,dv = \int_{p_A}^{p_B}\left(\frac{\Delta v}{\Delta t}\right)_p dt\,dp;$$

or differentiating,

$$dH = T\left(\frac{\Delta p}{\Delta t}\right)_v dt = T\left(\frac{\Delta v}{\Delta t}\right)_p dp,$$

$$H = T\int_A^{v_B}\left(\frac{\Delta p}{\Delta t}\right)_v dv = T\int\left(\frac{\Delta v}{\Delta t}\right)_p dp. \quad . \quad (19)$$

We see, then, that, if heat is added to any substance along an isothermal, the quantity of this heat can be represented by either of the two quantities in equation (19).

---

* This form is chosen to clearly indicate that we wish to obtain a number (or an expression) giving the ratio of the simultaneous changes of p and T at constant volume, and this in no way depends on the value of dt.

Prob. 31.—Prove from equation (19) that if heat is added to air at constant temperature, the heat required is $RT \log_e \frac{v_B}{v_A}$.

For air $pv = RT$ and $\left(\frac{\Delta p}{\Delta t}\right)_v = \left(\frac{dp}{dt}\right)_v$, from this equation, gives

$$vdp = Rdt,$$

$$\left(\frac{dp}{dt}\right)_v = \frac{R}{v}.$$

From equation (19),

$$H = \int_{v_A}^{v_B} T\frac{R}{v}dv.$$

As the temperature is to be constant, we have

$$H = RT \log_e \frac{v_B}{v_A}.$$

Prob. 32.—How much heat must be added at constant temperature to a substance whose equation is

$$p = 10^{6.1 - \frac{2730}{T}}$$

to change its volume at constant temperature from v_1 to v_2?

Prob. 33.—Having given

$$p = \frac{AT}{v} - \frac{B}{Tv^2}$$

as the relation between the pressure, volume, and temperature of a substance, how much heat must be added at constant temperature to change its volume from v_1 to v_2, having given the values of A, B, p_1, and T?

If, however, the heat, instead of being added along an isothermal, is added along any other line, the following method will determine the quantity of heat. Let AB (Fig. 16) be the line of the expansion, the co-ordinates being p and v. Let A and C be points dt degrees apart. The heat added between the points A and C is represented

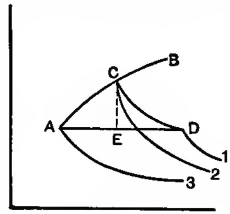

FIG. 16.

by the area $A32C$, and this area $= dH$. Through C draw the isothermal CD until it cuts the line of constant pressure through A. The heat added from A to C is equal to that added from A to D, minus that from D to C. Or, it is more nearly true to say that the latter quantity becomes more and more nearly equal to the heat added from A to C, as the temperature difference between A and C becomes smaller. Calling the difference in temperature dt, then AD is $\left(\frac{\Delta v}{\Delta t}\right)_p dt$, and CE is dp, as the point C is fixed by the intersection of the isothermal dt degrees above A and the given curve of expansion AB. The area $3AD1$ is the heat added from A to D, or is by definition $c_p dt$. The heat from D to C is the area $21DC$, or, from page 33, is $T\left(\frac{\Delta v}{\Delta t}\right)_p dp$, and we have taken this form because AD or dv is the quantity fixed by the two isothermals dt degrees apart. The heat from A to C is

$$AC23 = AD13 - DC21 = c_p dt - T\left(\frac{\Delta v}{\Delta t}\right)_p dp = dH, \quad (20)$$

which is one form of the general thermodynamic equation.

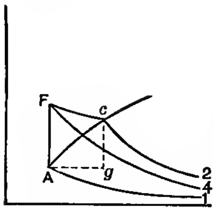

FIG. 17.

Another form of this equation is obtained as follows: Draw AF (Fig. 17) at constant volume until it cuts the isothermal through C. Then the area $1AC2$ differs from $1AF4 + 4FC2$ by the area AFC, which disappears as dt is made smaller. Then

$$Ag = dv, \qquad AF = \left(\frac{\Delta p}{\Delta t}\right)_v dt,$$

and we have the areas

$$AF41 = c_v dt, 4FC2 = T\left(\frac{\Delta p}{\Delta t}\right)_v dv,$$

and

$$dH = c_v dt + T\left(\frac{\Delta p}{\Delta t}\right)_v dv, \quad . \quad . \quad . \quad . \quad (21)$$

which is a second form of the fundamental equation. In these two equations the terms $\frac{\Delta p}{\Delta t}$ and $\frac{\Delta v}{\Delta t}$ depend only on the equation of the substance, and could have been written $\frac{dp}{dt}$ and $\frac{dv}{dt}$, while the other terms depend on the law of the expansion. That is, in the first one we have made dt and dp depend on the law which we have chosen to assume for the expansion, but the value $\frac{\Delta v}{\Delta t}$ depends only on the substance which is to

expand. In using these formulæ it must be remembered that the units must be the same for all the terms. That is, if the area $dp\,dv$ is in foot-pounds, it represents a certain part of the diagram, and the c_p or c_v must be in foot-pounds also; or if c_p and c_v are in heat-units, the value of $dp\,dv$ must be in heat-units also.

Prob. 34.—Suppose that there is a substance which, in the state we propose using it, is a gas, and that the relation between its pressure, temperature, and volume, as determined by experiment, can be expressed by the equation $pv = AT - \frac{B}{T}$. What will it do under various methods of expanding it?

First calling p constant, we have

$$pdv = Adt + \frac{Bdt}{T^2},$$

or

$$\left(\frac{dv}{dt}\right)_p = \frac{A}{p} + \frac{B}{T^2p};$$

and calling v constant,

$$\left(\frac{dp}{dt}\right)_v = \frac{A}{v} + \frac{B}{T^2v},$$

and the two forms of the fundamental equation are therefore

$$dH = c_v dt - \left(\frac{AT}{p} + \frac{B}{Tp}\right)dp, \quad . \quad . \quad . \quad . \quad . \quad (A)$$

$$dH = c_v dt + \left(\frac{AT}{v} + \frac{B}{Tv}\right)dv. \quad . \quad . \quad . \quad . \quad . \quad (B)$$

If now the substance is to expand at constant volume, we have, from (B), $H = c_v dt$. If at constant

pressure, from (A), $H = c_p dt$. If at constant temperature, from (A),

$$dH = -\left(AT + \frac{B}{T}\right)\frac{dp}{p}.$$

$$H = -\left(AT + \frac{B}{T}\right)\int\frac{dp}{p}, \text{ or, from (B)},$$

$$H = \left(AT + \frac{B}{T}\right)\int\frac{dv}{v}.$$

If it is to expand adiabatically, we have $dH = 0$ for both equations and $\frac{c_p}{c_v} = \frac{-\frac{dp}{p}}{\frac{dv}{v}}$, which is in the same form as the equation for the adiabatic expansion of air.

In using the fundamental formula we must remember that the formula gives us the heat added from A to B in the figures, and that when we speak of the *heat in a substance* we are measuring for some datum. Ordinarily this is taken at 32 degrees F., and, as this is the temperature at which a change of state in water takes place, we must define more particularly, so that if we are dealing with water or its vapor it is customary to measure the heat from that in water at 32 degrees.

Heat in Water and Steam.—The application of the general formula to the heat in a liquid and its vapor is as follows: When heat is added to a liquid (water, for instance) at 32 degrees, its temperature rises and its volume changes slightly. This continues until the temperature reaches such a point that vapor begins to

form. This is always a definite point for a given pressure. For water, 15 pounds pressure and 213 degrees correspond, 100 pounds pressure and 327 degrees; for ammonia, 37.8 pounds pressure and 10 degrees, 180 pounds pressure and 90 degrees, etc. The addition of any further quantity of heat to the liquid which is ready to boil does not increase the temperature, but vapor begins to form, part of the heat being used up in increasing the volume, and part in some sort of internal work required to change the liquid water into vapor. This condition of affairs continues until sufficient heat has been added to convert all the liquid into vapor. Any further addition of heat again raises its temperature and continues to increase the volume.

The addition of heat, therefore, at constant pressure takes place in three successive stages: first, while it is entirely a liquid; second, while part is liquid and part vapor; and third, after it is entirely a vapor. We have generally

$$dH = c_v dt + T\left(\frac{dp}{dt}\right)dv.$$

While it is a liquid v is practically constant and $dH = c_v dt$, $H = c_v(T_1 - T_{32})$ and is called q, or the heat of the liquid.

In reality there is a certain amount of work done and dv is not strictly zero, but the ordinary value of the specific heat of liquids includes the very small amount of heat necessary to do the external work.

c_v is not necessarily constant and $\int c_v dt$ is not necessarily equal to $c_v(T_1 - T_{32})$. If we know the relation

between c_v and T, it should be inserted before integrating and the exact value found. It is customary to say that for water $c_v = 1$, while in reality $c = 1 + .00004t + .0000009t^2$, t being in the centigrade scale, and we have

$$H = q = \int_0^t c\,dt = \int_0^t (1 + .00004t + .0000009t^2)dt$$
$$= t + .00002t^2 + .0000003t^3,$$

which is the true value of the heat of the liquid in French units. To get the corresponding quantity in English units, enter this equation with the centigrade temperature, and $\frac{9}{5}$ the value of the quantity obtained is the value in B.T.U. for the corresponding Fahrenheit temperature.

Prob. 35.—The specific heat of liquid anhydrous ammonia is given by the equation (French units)

$$c = 1.006 + .0037t.$$

How much heat must be added to 1 kilogram to raise its temperature from 20 to 40 degrees C.?

Prob. 36.—What is the specific heat of liquid ether at 30 degrees C. if the equation for q (French units) is

$$q = .529t + .0003t^2\,?$$

Prob. 37.—How much heat is required to raise 1 pound of water from 60 to 160 degrees F., using the specific heat of water?

Prob. 38.—What will be the temperature of 1 pound of water at 60 degrees if 10 heat-units are added to it?

Prob. 39.—Using the data of problem (34), how much heat must be added to 1 pound of liquid ether to raise its temperature from 40 to 50 degrees F.?

It is interesting to note just what proportion of this value of q is actually used for heating and what proportion goes to do outside work, because the part that does work may or may not be available if, for any reason, we have to make use of the heat in the water.

One pound of water at 50 degrees occupies .016 cubic foot.

One pound of water at 140 degrees occupies .01627 cubic foot.

The amount of work done if the water is under, say, 100 pounds pressure per square inch is $.00027 \times 100 \times 144 = 3.89$ foot-pounds, or .005 heat-units. The total heat required to raise 1 pound of water from 50 degrees F. to 140 degrees F. is 90.1 heat-units, or a practically negligible amount is used for doing work and we can say that all the heat added while it is still a liquid remains in it.

When the water reaches the boiling-point the temperature no longer rises, and we must again apply our general formula, as the conditions under which it was originally applied no longer hold. We have

$$dH = c_v dt + T\left(\frac{dp}{dt}\right)_v dv.$$

Now

$$dt = 0 \quad \text{and} \quad H = \int T\left(\frac{dp}{dt}\right)_v dv = r,$$

the total latent heat, as it is called. As T is constant, we could have written

$$r = T\int\left(\frac{dp}{dt}\right)_v dv \quad . \quad . \quad . \quad . \quad (22)$$

To apply this formula it is necessary to know the relation between p and t for the vapor to determine the value of $\left(\frac{dp}{dt}\right)_v$, and it is also necessary to know the limiting values of v. Experimentally, the relation between p and t can be easily obtained. The value of v when the liquid is all vapor is difficult to determine experimentally, and as r can be determined readily by experiment, this formula is of more value in determining the limiting value of v than in determining the value of r. In applying the formula either way, we know that $\frac{dp}{dt}$ does not depend on dv, as for each pressure there is a definite temperature and the equation might have been written

$$r = T\left(\frac{dp}{dt}\right)\int dv = T\left(\frac{dp}{dt}\right)(v_2 - v_1),$$

where v_2 is the volume of 1 pound of vapor, and v_1 the volume of 1 pound of liquid.

Prob. 40.—What is the volume of 1 pound of saturated steam at 100 pounds pressure per square inch if $r = 1113.9 - .695t$, and

$$p_{99} = 99 \times 144, \quad T_{99} = 326.86 + 460.7,$$
$$p_{100} = 100 \times 144, \quad T_{100} = 327.58 + 460.7,$$
$$p_{101} = 101 \times 144, \quad T_{101} = 328.30 + 460.7,$$

$$\Delta p = p_{101} - p_{99} = 2 \times 144,$$
$$\Delta T = T_{101} - T_{99} = 1.44,$$
$$r_{100} = 1113.9 - .695 \times 327.58 = 884.$$

From the formula $r = T\frac{\Delta p}{\Delta t}(v_2 - v_1)$ we have

$$884 \times 778 = 788.28 \times \frac{2 \times 144}{1.44}(v_2 - v_1),$$

or $$v_2 - v_1 = \frac{884 \times 778 \times 1.44}{2 \times 144 \times 788.28} = 4.36$$

and $$v_2 = 4.36 + .016 = 4.38.$$

Prob. 41.—What is the volume of 1 kilogram of saturated vapor of ether at 50° C., using the first five columns of Table IV, Peabody?*

Prob. 42.—What is the value of r in English units for carbon bisulphide at 50° F., using only columns 1, 2, 3, 9, 10, 11 of Table VII, Peabody?

Rankine gives $\log p = A - \frac{B}{T} - \frac{C}{T^2}$ for the relation between the pressure and the temperature, and the above equation can be written

$$r = p(v_2 - v_1)\left[\frac{B}{T} + \frac{2C}{T^2}\right].$$

Regnault's experiments give the following for the relation between the latent heat and the temperature:

$$r = 1113.9 - .695t;$$

and Peabody has deduced constants for Regnault's formula in the form of $\log p = a - b\alpha^n + c\beta^n$ for the relation between pressure and temperature which can be used for determining the value of $v_2 - v_1$.

The value of r above given consists of two parts, one of which does external work and the other internal

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* Peabody's Tables of the Properties of Saturated Steam and other Vapors.

work. Calling u the difference in volume $v_2 - v_1$, p the pressure, and A the heat equivalent of work, the external work is Apu, and the internal is $r - Apu = \rho$. The relations between ρ and Apu are very different from the corresponding quantities while in a liquid state, as the Apu is about $\frac{1}{10}\rho$.

It is to be remembered that the external work has been done, and while the heat to do it has been expended, this heat no longer exists in the steam formed. It may have been expended in pumping water, and may exist as potential energy stored in water in some distant reservoir. That is, r has been expended and ρ remains in the vapor, and the Apu is not in the steam and *is not* available for any future work. When the pound of water at 32° F. is heated and entirely evaporated under constant pressure, we have added to it $q + r = \lambda$ heat-units, and this is called the total heat. It is often written as total heat "in the steam." This expression is incorrect, as it is the total heat required to form the steam. The amount of heat "in the steam" is only $q + \rho$.

The steam being entirely formed, the addition of more heat at constant pressure superheats it, and it has been found that the specific heat of superheated steam at constant pressure is .48. That is, if the steam is raised t degrees above its point of saturation the heat added is $.48t = c_p(T_{\text{sup.}} - T_{\text{sat.}})$.

Of this heat added, only a portion remains in the steam. A certain amount of external work must be done, and while we have expended $.48(T_{\text{sup.}} - T_{\text{sat.}})$ heat-units, a quantity of work has been done equal to

$p(v_{\text{sup.}} - v_{\text{sat.}})$. The heat remaining in the steam is therefore

$$.48(T_{\text{sup.}} - T_{\text{sat.}}) - p(v_{\text{sup.}} - v_{\text{sat.}}).$$

To determine the value of this quantity we must have the relation between the pressure, volume, and temperature of superheated steam.

This relation determined experimentally can be expressed by the following equation (Peabody):

$$pv = 93.5T - 971p^{\frac{1}{4}},$$

from which either T or v can be readily found if the remaining two quantities are given. In tabular form we then have, starting with water at 32 degrees and ending at the state given below:

ALL LIQUID.

Heat added $= q$;
Heat remaining $= q$.

MIXTURE OF LIQUID AND VAPOR.

($x =$ parts vapor.)

Heat added $= q + xr$;
Heat remaining $= q + x\rho$;
Work done $= xApu$.

ALL VAPOR.

Heat added $= q + r + .48(T_{\text{sup.}} - T_{\text{sat.}})$;
Heat remaining

$$= q + \rho + .48(T_{\text{sup.}} - T_{\text{sat.}}) - p(v_{\text{sup.}} - v_{\text{sat.}});$$

Work done $= Apu + p(v_{\text{sup.}} - v_{\text{sat.}})$.

Prob. 43.—How much external work is done in converting 1 pound of water at 60 degrees into a mixture having $x = .6$ at 150 pounds pressure?

How much heat is expended?

Prob. 44.—How much heat is in 1 pound of superheated steam at 150 pounds pressure and 400 degrees F., counting from 32 degrees, and how much work has been done?

Prob. 45.—If 80,000 foot-pounds of external work is done in converting 1 pound of water into steam at 150 pounds pressure, what must be the condition of the steam?

The distinction between the heat added and the heat remaining in a substance can be perhaps better understood by the following example: Suppose B (Fig. 18) is the initial state of 1 pound of water at 15 pounds pressure and 213 degrees F., and A is its final condition at 100 pounds pressure and 327.58 degrees F. At B the water has in it $q = 181.8$ heat-units. At A it will have in it as steam

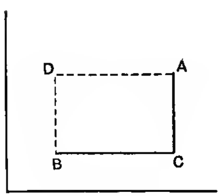

FIG. 18.

$$q + \rho = 297.9 + 802.8 = 1100.7.$$

To pass from B to A we must do a certain amount of work. The difference in volume between B and A is 4.387 cubic feet.

Suppose that the volume A is first filled at 15 pounds pressure, and that afterwards heat is added and the

pressure is raised to 100 pounds from C to A: the amount of work done is equal to

$$\frac{15 \times 144 \times 4.387}{778} = 12.2 \text{ heat-units.}$$

The total heat that must be expended is therefore

$$1100.7 + 12.2 - 181.8 = 931.1 \text{ heat-units.}$$

Suppose again that the pressure is first raised to D and the volume is then increased to A. The work done in this case is equal to

$$\frac{100 \times 144 \times 4.387}{778} = 81.2 \text{ heat-units,}$$

and the heat required is

$$1100.7 + 81.2 - 181.8 = 1000.1.$$

It is therefore to be noted that the amount of heat which must be expended depends upon the way in which it is expended, but that the portion of the heat added which remains in the substance is, in the example above given, always

$$1100.7 - 181.8 = 918.9 \text{ heat-units,}$$

or

$$q_{100} + \rho_{100} - q_{15}.$$

Prob. 46.—Four pounds of a mixture of steam and water at 60 pounds pressure per square inch fill a vessel A of 10 cubic feet capacity, and 6 pounds of mixture fill another vessel, B, of 10 cubic feet at 100 pounds pressure. If the contents of the two vessels are intimately mixed, the volume not changing, what will be the final pressure, assuming no radiation?

First determine the heat in vessel A. We have

$$4x \times 7.096 + 4(1 - x).016 = 10, \quad x = .35.$$

$$\text{Heat} = 4(261.9 + .35 \times 830.7) = 2212.$$

To determine the heat in vessel B:

$$6x \times 4.403 + 6(1 - x).016 = 10, \quad x = .376.$$

$$\text{Heat} = 6(297.9 + .376 \times 802.8) = 3600,$$

The heat per pound of the mixture is then

$$\frac{2212 + 3600}{10} = 581.2,$$

and the volume occupied per pound is $\frac{20}{10} = 2$ cubic feet. We have then two equations to satisfy:

$$x \times s + (1 - x).016 = 2,$$
$$q + x\rho = 581.2,$$

and these can best be solved by trial.

Prob. 47.—What heat must be added at constant volume to raise the pressure of one pound of a mixture of steam and water occupying 3.8 cubic feet from 100 to 150 pounds pressure per square inch?

Prob. 48.—A vessel of 10 cubic feet capacity has in it 4 pounds of a mixture of steam and water at 100 pounds pressure; 25 pounds of water at 60 degrees F. are pumped into the vessel. What is the resulting temperature, assuming no radiation?

Prob. 49.—If 10 cubic feet of dry saturated steam at 100 pounds pressure per square inch is allowed to pass from a

boiler into an open vessel having in it 25 pounds of water at 60 degrees F., what is the resulting temperature?

Adiabatics.—We have already proved that if a substance expands at constant temperature between two adiabatics, the heat added divided by the temperature is constant. To repeat in a slightly different form, let the diagram, Fig. 19, be a heat diagram, in which AB and EF are constant-temperature lines, and AC and BD are two adiabatics. Then the area $ABDC$ divided by

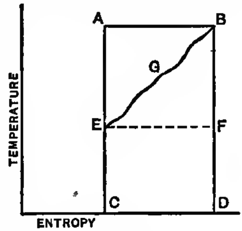

FIG. 19.

$T_A =$ area $EFDC$ divided by T_E, or $\dfrac{H_{AB}}{T_A} = \dfrac{H_{EF}}{T_E}$ directly from the figure. We can also write

$$\int_B^A \frac{dH}{T} = \int_F^A \frac{dH}{T} = \int_B^E \frac{dH}{T},$$

as each of these quantities is the horizontal distance between the lines AC and BD. That is, it makes no difference how much heat is added between E and B, for instance, nor how it is added, the quantity $\int \dfrac{dH}{T}$ is constant and, if we please, is equal to $\dfrac{H_{EF}}{T_E}$ or $\dfrac{H_{AB}}{T_A}$ or is equal to $\displaystyle\int_E^B \frac{d(H_{EGB})}{T}$, the T in the latter case being a variable, and is the temperature at which $d(H_{EGB})$ is added.

Along the adiabatic, as $dH = 0$, we have $\int \frac{dH}{T} = 0$.

The statement that $\int \frac{dH}{T}$ is constant between two adiabatics for any substance gives us another method of obtaining the equation to the adiabatic for air. In Fig. 20 suppose a to be a point on one adiabatic, and b and c points on another.

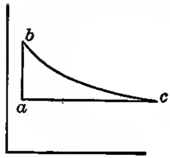

FIG 20.

As $\int \frac{dH}{T}$ is constant from a to b, or to c, suppose ab to be a constant-volume line and ac a constant-pressure line.

We have for ab

$$\int \frac{dH}{T} = \int_{T_a}^{T_b} \frac{c_v dt}{T} = c_v \log_e \frac{T_b}{T_a},$$

for ac

$$\int \frac{dH}{T} = \int_{T_a}^{T_c} \frac{c_p dt}{T} = c_p \log_e \frac{T_c}{T_a},$$

and

$$c_v \log_e \frac{T_b}{T_a} = c_p \log_e \frac{T_c}{T_a};$$

$$\left(\frac{T_b}{T_a}\right) = \left(\frac{T_c}{T_a}\right)^{\frac{c_p}{c_v}} = \left(\frac{T_c}{T_a}\right)^{1.41};$$

or, as $pv = RT$,

$$\frac{p_b v_b}{p_c v_b} = \frac{p_c^{1.41} v_c^{1.41}}{p_c^{1.41} v_b^{1.41}},$$

or

$$p_b v_b^{1.41} = p_c v_c^{1.41},$$

which we have before deduced in an entirely different way.

When we come to apply this method to liquids and vapors the problem is rather more complicated. In Fig. 21 suppose a to represent the pressure and volume of 1 pound of water, and suppose the temperature to be T_1. Let bc be an adiabatic curve such that at b we have x_b pounds of steam and $1 - x_b$ pounds of water, and suppose that at c we have x_c pounds of steam and $1 - x_c$ pounds of water. We know that

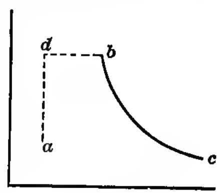

FIG. 21.

$$\int_a^b \frac{dH}{T} = \int_a^c \frac{dH}{T}$$

from what has just been proved.

On the path from a to b suppose first the temperature is raised to d, and then that x_b pounds of steam are made. From a to d, $dH = cdt$, because in the general formula,

$$dH = c_v dt + T\left(\frac{dp}{dt}\right)dv,$$

we have $dv = 0$, and hence $\int_a^d \frac{dH}{T} = \int_{T_a}^{T_d} \frac{cdt}{T}$.

From d to b the heat dH added is rdx, and we can write

$$\int_d^b \frac{dH}{T} = \int_0^{x_b} \frac{r_b dx}{T_b} = \frac{r_b x_b}{T_b}$$

and

$$\int_a^b \frac{dH}{T} = \int_{T_a}^{T_b} \frac{cdt}{T} + \frac{x_b r_b}{T_b}.$$

From a to c we can write

$$\int_a^c \frac{dH}{T} = \int_{T_a}^{T_c} \frac{cdt}{T} + \frac{x\, r_c}{T_c},$$

and as these are equal, we can write

$$\int_{Ta}^{T_b} \frac{cdt}{T} + \frac{x_b r_b}{T_b} = \int_{Ta}^{T} \frac{cdt}{T} + \frac{x_c r_c}{T_c} \quad . \quad . \quad (23)$$

In this equation c is the specific heat of water, or is $\frac{dq}{dt}$, and if we know one value of x, we can determine any other. Ordinarily the value of $\int \frac{cdt}{T}$ can be calculated with sufficient accuracy by calling $c = 1$, and $\int \frac{cdt}{T}$ is then $c \log_e \frac{T_d}{T_a}$; but Peabody's tables give the value of this quantity using the exact value of c, so that it need not be calculated.

Prob. 50.—If 1 pound of a mixture of steam and water occupying 3.8 cubic feet at a pressure of 100 pounds absolute expands adiabatically to 15 pounds pressure, what is its volume?

We have from the steam-table

$T_{100} = 327.58 + 460.7$; Vol. 1 lb. steam$_{100} = 4.403$ cu. ft.; $r_{100} = 884$.

Calling $T_a = 32° + 460.7$, we have

$$\int \frac{cdt}{T} = 2.3026 \, (\log 788.28 - \log 492.7) = .470$$

approximately, or .4733 from the tables.

$T_{16} = 213.03 + 460.7$; Vol. 1 lb. steam$_{16} = 26.15$ cu. ft.;

$$r_{15} = 965.1; \quad \int \frac{cdt}{T} = .3143.$$

To determine x_b we have, as .016 is the volume of a pound of water,

$$(1 - x_b) \, .016 + x_b \, 4.403 = 3.8 \, ;$$

$$x_b = .861.$$

We can then write

$$\int_{T_{32}}^{T_{100}} \frac{cdt}{T} + \frac{.861 \times 884}{788.28} = \int_{T_{32}}^{T_{16}} \frac{cdt}{T} + \frac{x_c 965.1}{673.73} \, ;$$

$$.4733 + .964 = .3143 + 1.431 x_c \, ;$$

$$x_c = .782 \, ;$$

$$\text{Vol.} = .782 \times 26.15 + (1 - .782) \, .016 = 20.5 \text{ cu. ft.}$$

Prob. 51.—If 1 pound of a mixture containing 40 per cent of water is compressed adiabatically from 20 to 60 pounds pressure, what is the percentage of moisture at the higher pressure?

Prob. 52.—A pound of a mixture is expanded adiabatically, so that it has the same percentage of water at 60 and 15 pounds. What must have been the percentage at 60 pounds pressure?

Whenever a body expands adiabatically, or at the expense of its own heat, the amount of external work done must be the difference in the quantity of heat in it at the beginning and at the end of the expansion.

If we have a mixture of steam and water at the beginning of the expansion so that the portion of steam is x_1, the heat present is $q_1 + x_1\rho_1$. At the end of the expansion the heat is $q_2 + x_2\rho_2$, and the amount of work done is therefore

$$q_1 + x_1\rho_1 - q_2 - x_2\rho_2.$$

Prob. 53.—In problem (50) how much work is done in the expansion?

From the tables

$$q_1 = 297.9, \quad \rho_1 = 802.8,$$

$$q_2 = 181.8, \quad \rho_2 = 892.6, \quad \text{and}$$

the work $= 297.9 + .861 \times 802.8 - 181.8 - .782 \times 892.6 = 107$ h. u.,

or $107 \times 778 = 83200$ ft.-lbs.

Prob. 54.—What work is done if 20 cubic feet of a water mixture weighing 6 pounds expands adiabatically from 80 pounds to 20 pounds pressure?

Prob. 55.—1 pound of steam at 100 pounds pressure expands adiabatically to 15 pounds. How much work is done?

Prob. 56.—1 pound of water at 327 degrees F. expands adiabatically to 15 pounds pressure. How much work is done?

If we are dealing with superheated steam instead of a mixture, we have for the value of $\int \frac{dH}{T}$ three parts:

one while it is still a liquid or $\int \frac{cdt}{T}$, one while it is becoming steam at constant temperature, or $\frac{r}{T}$ (as it is all converted into steam), and a third portion,

$$\int_{T_{\text{sat.}}}^{T_{\text{sup.}}} \frac{c_p dt}{T} = c_p \log_e \frac{T_{\text{sup.}}}{T_{\text{sat.}}},$$

and we can write

$$\int \frac{dH}{T} = \int \frac{cdt}{T} + \frac{r}{T} + c_p \log_e \frac{T_{\text{sup.}}}{T_{\text{sat.}}} . \qquad (24)$$

When superheated steam expands adiabatically, we have, for the amount of work done, the difference in the quantity of heat at the beginning and end of expansion.

The heat at the beginning is

$$q_1 + \rho_1 + \left[c_p (T_{\text{sup.}} - T_{\text{sat.}}) - \frac{p_1 (V_{\text{sup.}} - V_{\text{sat.}})}{778} \right].$$

The heat at the end of expansion is

$$q_2 + \rho_2 + \left[c_p (T_{\text{sup.}} - T_{\text{sat.}}) - \frac{p_2 (V_{\text{sup.}} - V_{\text{sat.}})}{778} \right]$$

on the assumption that it remains superheated until the end of the expansion.

Prob. 57.—1 pound of steam at 150 pounds pressure occupies a volume of 3.3 cubic feet. What is its condition after it expands adiabatically to 15 pounds pressure, and what work is done?

As 1 pound of saturated steam at 150 pounds pressure occupies 3.011 cubic feet, the steam in the problem must be superheated, and from the equation of superheated steam we have

$$T = \frac{pv + 971p^{\frac{1}{4}}}{93.5},$$

or

$$T = \frac{150 \times 144 \times 3.3 + 971 \times (150 \times 144)^{\frac{1}{4}}}{93.5} = 890^\circ.$$

Saturated steam at 150 pounds pressure has a temperature of 358.26 degrees F. = 818.96, or the steam is superheated 71 degrees. We have then

$$\int \frac{dH}{T} = \int \frac{cdt}{T} + \frac{r}{T} + c_p \log_e \frac{890}{819}$$

$$= .5133 + \frac{861.2}{819} + .48 \times 2.3026 \log \frac{890}{819}$$

$$= .5133 + 1.0525 + 0.397$$

$$= 1.6055.$$

At 15 pounds pressure

$$\int \frac{cdt}{T} = .3143, \quad \frac{r}{T} = \frac{965.1}{673.73} = 1.433.$$

As the sum of these two $= 1.7473$ is greater than 1.6055, the steam is evidently not superheated at the lower pressure and we have

$$1.6055 = .3143 + x \times 1.433,$$

$$x = .901.$$

To determine the amount of work done during this expansion, we have the heat at the initial condition

$$= q_{150} + \rho_{150} + \left[c_p(890 - 819) - \frac{150 \times 144}{778}(3.3 - 3.011) \right]$$

[Heat added less work done]

$$= 330 + 778.1 + 26.07 = 1134.17$$

At the final condition the heat in the steam is

$$q_{15}+.901\rho_{15} = 181.8+.901\times 892.6 = 985.03.$$

The work done is

$$1134.17 - 985.03 = 149.14 \text{ h. u.} = 116000 \text{ ft.-lbs.}$$

Prob. 58.—If in the above problem the volume had been 4 cubic feet at 150 pounds pressure, what would have been the condition and how much work would have been done if it had expanded to 15 pounds pressure?

Prob. 59.—If 1 pound of steam at 15 pounds pressure superheated 60 degrees is adiabatically compressed to 100 pounds pressure, what is its temperature and volume?

Curve of Constant Steam Weight.—If 1 pound of saturated steam expands in such a manner that we have always 1 pound of saturated steam whatever its pressure, the expansion curve is called a curve of constant steam weight. Or if a mixture of steam and water having a given proportion of steam expands in such a way that, whatever its pressure, there is always the same proportion of steam present, the curve of expansion is called a curve of constant steam weight.

Prob. 60.—If 1 pound of a mixture of steam and water at 120 pounds pressure expands so that 30 per cent is always steam, what are the volumes at 120, 90, 60, and 30 pounds pressure?

At 120 pounds we have for the volume of the steam $.30\times 3.711$, and for the water $.70\times .016$, and the total volume is $1.1133+.0112 = 1.1245$ cubic feet.

Prob. 61.—A mixture of 60 per cent steam and 40 per cent water expands from 90 to 15 pounds pressure, so that there is always 60 per cent steam. What is the volume at every 15 pounds pressure, if the total weight is 5 pounds?

To Determine the Work Done.—The amount of work done by such an expansion can only be approximately determined by calculation. The most convenient way of doing it is to assume that the expansion curve is in the form $pv^n = K'$, and find the most probable value of n, and from the equation of the curve determine the area.

To determine the most probable value of n, it is not correct to determine several values of n and average them. The following, from the method of least squares, gives the most probable value of n and is not at all difficult to follow out. Determine as many values of p and v as desired, and write these values in the logarithmic equation as below:

$$\begin{aligned} \log p_1 + n \log v_1 &= \log K' = K''; \\ \log p_2 + n \log v_2 &= \quad\quad K''; \\ \log p_3 + n \log v_3 &= \quad\quad K'', \text{ etc.} \end{aligned}$$

Add these equations together and we have

$$\Sigma \log p + n\Sigma \log v = \Sigma K'' . \quad . \quad . \quad . \quad . \quad \text{(A)}$$

Now multiply each of the original equations by the coefficient of n in that equation and we have

$$\begin{aligned} \log p_1 \log v_1 + n (\log v_1)^2 &= K'' \log v_1; \\ \log p_2 \log v_2 + n (\log v_2)^2 &= K'' \log v_2; \\ \log p_3 \log v_3 + n (\log v_3)^2 &= K'' \log v_3. \end{aligned}$$

Adding these equations together we have

$$\Sigma \log p \log v + n\Sigma (\log v)^2 = \Sigma K'' \log v. \quad . \quad \text{(B)}$$

Solving (A) and (B) will give the most probable value of n. Ordinarily three-place logarithms are not accurate enough for this work. The amount of work is then

$$W = \frac{p_1 v_1 - p_2 v_2}{1 - n}.$$

To determine the quantity of heat that will be required to produce this expansion, we know that the heat at the end of the expansion added to the work done must be equal to the heat in the steam at the beginning of the expansion added to the heat supplied. We have already shown how to determine three of these quantities so that the heat supplied can be determined.

Prob. 62.—1 pound of steam at 60 pounds pressure expands to 40 pounds along a curve of constant steam weight. How much work is done and how much heat must be supplied? We have the following for the pressures and volumes:

$$\begin{aligned} \text{At 60 lbs. } V &= 7.096 \text{ cu. ft.;} \\ \text{50 lbs. } V &= 8.414 \text{ cu. ft.;} \\ \text{40 lbs. } V &= 10.37 \text{ cu. ft.} \end{aligned}$$

To determine the law of expansion write:

$$\begin{array}{ll} \log p + n \log v = K'' & \\ 1.778 + .851n = K'' & 1.513 + .724n = .851K'' \\ 1.699 + .925n = K'' & 1.572 + .856n = .925K'' \\ 1.602 + 1.016n = K'' & 1.628 + 1.032n = 1.016K'' \\ \hline 5.079 + 2.792n = 3K'' \quad \text{(A)} & 4.713 + 2.612n = 2.792K'' \quad \text{(B)} \end{array}$$

$$n = 1.07.$$

$$\text{Work} = \frac{60 \times 144 \times 7.096 - 40 \times 144 \times 10.37}{1.07 - 1} = 21500 \text{ ft. lbs.}$$

$$\text{Heat required} = q_{40} + \rho_{40} + \frac{21500}{778} - q_{60} - \rho_{60}.$$

$$236.4 + 850.3 + 27.6 - 261.9 - 830.7 = 21.7 \text{ h. u.}$$

Rectangular Hyperbola.—In many cases a rectangular hyperbola practically represents the expansion taking place in a mixture of steam and water under actual conditions. This is in no sense a theoretical expansion line for a steam expansion, but it practically represents what actually takes place in many steam-engine cylinders. The law of the expansion here is $pv = K$, and the amount of work done is

$$p_1 v_1 \log_\epsilon \left(\frac{v_2}{v_1}\right) = p_1 v_1 \log_\epsilon \left(\frac{p_1}{p_2}\right).$$

The amount of heat required is

$$q_2 + x_2 \rho_2 + p_1 v_1 \log_\epsilon \left(\frac{p_1}{p_2}\right) - q_1 - x_1 \rho_1,$$

the subscript 2 referring to the final condition, and 1 to the initial condition.

Prob. 63.—1 pound of a water mixture containing 30 per cent of moisture expands from 100 pounds to 20 pounds, so that 30 per cent of moisture is always present. How much work is done, and must heat be added or taken away, and how much?

Prob. 64.—1 pound of a mixture containing 30 per cent of moisture expands from 100 pounds to 30 pounds along a rectangular hyperbola. How much work is done, what is the condition at the end of the expansion, and how much heat must be added or taken away?

CYCLES PASSED THROUGH BY VAPORS.

When a vapor is used in a cylinder the amount of work done and the amount of heat required can be determined as follows: Suppose that at a, Fig. 22, we have 1 pound of a mixture of vapor and liquid, x_a parts being vapor, and suppose that, at b, x_b parts are vapor, the pressure remaining constant.

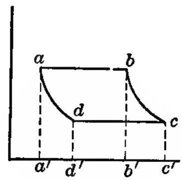

FIG. 22.

From b to c let the expansion be according to any law, and at c let x_c be the proportion of the vapor. Let heat be taken away first at constant pressure, and then according to the same law as the expansion curve bc, so that we have at the end of the cycle the same condition of affairs as at the beginning.

The amount of work done is the area of the figure $abcd$. It can be most easily calculated by finding the separate areas and combining them so that

$$W = abb'a' + bcc'b' - cdd'c' - add'a'.$$

The area $abb'a' = (x_b - x_a)Ap_a u_a$.

The area $cdd'c' = (x_c - x_d)Ap_c u_c$.

The areas under bc and ad depend upon the law of the expansion and can be determined as shown before.

The amount of heat required to do this work is the heat required from a to c and is equal to

$$(q_c + x_c\rho_c) - (q_a + x_a\rho_a) + abcc'a'.$$

The amount of heat which must be taken away is

$$-(q_a + x_a\rho_a) + adcc'a' + (q_c + x_c\rho_c).$$

The relation between the various values of x depends on the law of the expansion.

If the expansion is adiabatic, the value of x_c and x_d can be determined if x_a and x_b are given. We have

$$\int_c^b \frac{cdt}{T} + \frac{x_b r_b}{T_b} = \frac{x_c r_c}{T_c},$$

all the terms of which are known except x_c; and

$$\int_d^a \frac{cdt}{T} + \frac{x_a r_a}{T_a} = \frac{x_d r_d}{T_d},$$

from which x_d can be determined.

As r_b and T_b are equal to r_a and T_a, and similarly for c and d, we can write from the last two equations

$$\frac{r_a}{T_a}(x_b - x_a) = \frac{r_c}{T_c}(x_c - x_d).$$

The work done can then be written

$$W = Ap_b u_b(x_b - x_a) + [q_b + x_b\rho_b - q_c - x_c\rho_c]$$
$$- Ap_c u_c(x_c - x_d) - [q_a + x_a\rho_a - q_d - x_d\rho_d]$$
$$= x_b r_b - x_a r_b - x_c r_c + x_d r_c$$
$$= (x_b - x_a)r_b - (x_c - x_d)r_c$$
$$= (x_b - x_a)\left(r_b - \frac{T_c r_a}{T_a}\right)$$
$$= (x_b - x_a)r_a\left(\frac{T_a - T_c}{T_a}\right).$$

In the last equation $(x - x_a)\, r_a$ is the heat added from a to b. The efficiency is therefore $\frac{T_a - T_c}{T_a}$, which is Carnot's efficiency, as might have been expected as this is a Carnot cycle. When this condition of affairs exists in a cylinder, the cylinder fulfils the functions of boiler, engine, and condenser, as we have assumed that the given weight of the substance is in the cylinder at all the points of the cycle.

Prob. 65.—How much work is done in the cycle of Fig. 22, if 5 pounds of a mixture of steam and water expands having $p_a = 100$ pounds per square inch, $p_d = 15$ pounds per square inch, $x_a = .1$, $x_b = .9$?

From the tables

$$r_a = 884.0 \text{ h. u.}; \quad T_a = 788.3; \quad T_d = 673.7.$$

The heat added from a to b is

$$M(x_b - x_a)r_a = 5 \times (.9 - .1) \times 884.0 = 3536 \text{ h. u.}$$

The work done is

$$\frac{788.3 - 673.7}{788.3} \times 3536 \times 778 = 402000 \text{ ft.-lbs.}$$

Prob. 66.—1 pound of NH_3 expands through a cycle, as in Fig. 22. If $t_a = 60$ degrees F., $t_d = 10$ degrees F., $x_a = .1$, $x_b = 1$, how much work is done and how much heat is required?

Prob. 67.—If in a cycle, like Fig. 22, $v_c = 10$ cubic feet, $v_a = 1$ cubic foot, $p_a = 150$ pounds per square inch, $p_c = 15$, how much work is done and how much heat is required if 1 pound of steam is used?

In an actual engine the conditions are different from those in the last figure, as from a to b there is not the same weight in the cylinder, and from c to d

the weight also varies. And in addition there is constant interchange of heat between the cylinder walls and the steam.

First, neglecting the action of the cylinder-walls, suppose Fig. 23 represents what takes place in the cylinder. At a the clearance volume is filled with steam whose steam proportion is x^a. The steam from the boiler is admitted and fills the cylinder to c. Expansion takes place to d, and exhausts to a again.

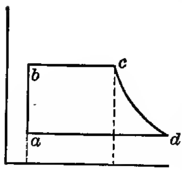

FIG. 23.

Let m pounds be in the cylinder at a, and M pounds be added from the boiler. Let x' be the value for the steam coming from the boiler. If we know the volume at c, we have $\frac{V_c}{m+M}=$ volume of 1 pound and

$$x_c s_c + (1 - x_c)\,.016 = \frac{V_c}{m+M},$$

from which x_c can be found.

To find the work from b to c we have that the heat at c added to the work done is equal to the heat at a added to the heat received from the boiler, or

$$(m+M)(q_c+x_c\rho_c)+\text{Work } bc=m(q_a+x_a\rho_a)+M(q_c+x'r_c).$$
$$\text{Work } bc = m(q_a + x_a\rho_a - q_c - x_c\rho_c) + M(x'r_c - x_c\rho_c).$$

We might have written

$$\text{Work } bc = (V_c - V_a)p_c,$$

but it has been written in the form first given to call attention to the fact that the last term in the first equation contains r_c and not ρ_c. The reason is that the heat brought into the cylinder from the boilers includes not only q_c and $x'\rho_c$, but also the external work which must be done in forcing this steam out of the boiler, or $x'Ap_cu_c$.

The work under cd is determined as before shown, and the work under da is the area of the rectangle under ad, or

$$(V_d - V_a)p_d.$$

Prob. 68.—In an engine having Fig. 23 for a card, let $V_a = .4$ cubic feet, $V_d = 8$ cubic feet, $p_b = 100 \times 144$, $p_a = 15 \times 144$, $x_a = .9$, $x_d = .8$, cd being an adiabatic. How much work is done?

First find x_c.

$$\int_{15}^{100} \frac{cdt}{T} + \frac{x_c r_{100}}{T_{100}} = \frac{.8 r_{15}}{T_{15}};$$

$$x_c = \frac{T_{100}}{r_{100}} \left[\frac{.8 r_{15}}{T_{15}} - \int_{15}^{100} \frac{cdt}{T} \right]$$

$$= \frac{788.3}{884} \left[\frac{.8 \times 965.1}{673.7} - .4733 + .3143 \right] = .88.$$

To find the volume at c we must know the weight along cd and we have

$$x_d m_d s_d + (1 - x_d) m_d .016 = 8.$$

From the tables $s_d = 26.15$;

$$m_d = \frac{8}{.8 \times 26.15 + .2 \times .016} = \frac{8}{20.952} = .381 \text{ lbs.};$$

$$V_c = .381(.88 \times 4.403 + .12 \times .016) = 1.47 \text{ cu. ft.}$$

The work $bc = (1.47 - .4)100 \times 144 \qquad = 15400$

The work $cd = .381[q_{100} + .88\rho_{100} - q_{15} - .8\rho_{15}] \times 778 = 32000$

47400

The work $da = (8 - .4)15 \times 144 \qquad = 16400$

Work in cycle $\qquad = 31000$

Prob. 69.—In the above problem, how much steam must the boiler have furnished if $x' = 1$?

Prob. 70.—How much steam was in the cylinder at b, and what was the value of x_b if there was no loss of heat through or to the cylinder-walls?

Prob. 71.—In problem 68, how much heat must have been taken up by the cylinder-walls if $x' = 1$ and $x_c = .88$?

If, instead of the exhaust continuing to a, it had stopped at e of Fig. 24, the above formula will apply by putting in the corresponding values of pressures and temperatures, etc., for the new point a, and the amount of work will be reduced by the area aef, which must be determined as already shown.

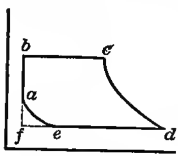

FIG. 24.

In all engines using vapors, the quantity of heat rejected along the line da of Fig. 23, or de of Fig. 24, is a large proportion of the total heat supplied to an engine. To use the same working substance over and over again in an engine, it must be liquefied, pumped into a boiler, and evaporated again. All the heat rejected from the engine less the amount which remains in the working substance as a liquid cannot be again utilized for doing work in the same engine. The quantity of heat which must be supplied to the working substance for each cycle is therefore the amount

which must be added to it as a liquid at the temperature of its discharge from the engine.

Prob. 72.—In Fig. 24, using steam, if $x_c = .7$, $m_c = 1$, $x_e = 1$, $m_e = .1$, $p_b = 100 \times 144$, $p_d = 15 \times 144$, $p_a = 30 \times 144$, the curves *cd* and *ea* are rectangular hyperbolas, how much work is done per cycle and how much heat is expended?

Prob. 73.—If, having given the data of problem 72, the substance is anhydrous ammonia, what work is done and how much heat is expended per cycle?

Prob. 74.—If, having given the data of problem 72, the substance is SO_2, what is the work done and what the heat expended per cycle?

When the action of the cylinder-walls is taken into account, the following analysis might be made after the method of Hirn. Assume that at *c*, Fig. 23, we have steam with a given proportion of moisture and that the expansion is a rectangular hyperbola, and assume further that saturated steam without moisture has been supplied, which is nearly true, and that the steam discharged is steam without moisture, which may or may not be true.

From *c* to *d* the cylinder-walls must give up heat per pound equal to

$$(q_d + x_d\rho_d) + p_c v_c \log_e \frac{V_d}{V_c} - (q_c + x_d\rho_c),$$

all the terms of which are known except x_d. This can be calculated from

$$x_d s_d + (1 - x_d)\,.016 = \frac{V_d}{m + M}.$$

From d to a the cylinder-walls must give up heat to the amount

$$m(q_a + x_a\rho_a) + M(q_a + r_a) - \frac{p_a(V_d - V_a)}{778} \\ - (m + M)(q_a + x_d\rho_d).$$

This is, of course, on the assumption that no heat is radiated. The amount radiated can be accounted for and the formula made exactly true.

Prob. 75.—Suppose we have, Fig. 23, volume $d = 7.2$ cubic feet, volume $a = .14$ cubic feet, volume $c = 1.08$ cubic feet; weight steam used $= .35$ pound; pressure $c = 100$, pressure $a = 15$; $x_c = .64$, $x_a = .9$. What should theoretically be the condition of the exhaust steam if the boiler supplies steam having $x' = 1$, and the expansion curve is a rectangular hyperbola, assuming no radiation from the cylinder.

The heat received from the boiler less that rejected to the condenser or air is the work done, as we have assumed no radiation.

The heat received is $M(q_c + r_c)$.

The work done is

$$100 \times 144 \times .88 + 100 \times 144 \times 1.08 \log_e \frac{7.20}{1.08} - 7.06 \times 144 \times 15$$
$$= 27000 \text{ ft.-lbs.} = 34.7 \text{ h. u.}$$

The heat rejected is $M(q_a + x_a r_a)$ and

$$M(q_a + x_a r_a) = M(q_c + r_c) - 34.7;$$

$$x_a = \frac{.35(q_c + r_c - q_a) - 34.7}{M r_a}$$

$$= \frac{.35(297.9 + 884 - 181.8) - 34.7}{.35 \times 965.1} = .931,$$

showing that under these conditions the exhaust steam will have 6.9 per cent moisture in it.

Prob. 76.—A condensing engine working between 150 and 4 pounds pressure requires 15 pounds of dry saturated steam per indicated horse-power per hour. If no heat is radiated from the cylinder, what must be the average condition of the exhaust?

Prob. 77.—Draw a diagram showing the quantity of dry saturated steam that must be used per horse-power per hour in order that the exhaust at 4 pounds pressure may be dry saturated steam, if the steam-pressure is 80, 100, 120, 140, and 160 pounds per square inch, there being no radiation.

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